

Photoassociation and coherent transient dynamics in the interaction of ultracold rubidium atoms with shaped femtosecond pulses - I. Experiment

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We experimentally investigate various processes present in the photoassociative interaction of an ultracold atomic sample with shaped femtosecond laser pulses. We demonstrate the photoassociation of pairs of rubidium atoms into electronically excited, bound molecular states using spectrally cut femtosecond laser pulses tuned below the rubidium D1 or D2 asymptote. Time-resolved pump-probe spectra reveal coherent oscillations of the molecular formation rate, which are due to coherent transient dynamics in the electronic excitation. The oscillation frequency corresponds to the detuning of the spectral cut position to the asymptotic transition frequency of the rubidium D1 or D2 lines, respectively. Measurements of the molecular photoassociation signal as a function of the pulse energy reveal a non-linear dependence and indicate a non-perturbative excitation process. Chirping the association laser pulse allowed us to change the phase of the coherent transients. Furthermore, a signature for molecules in the electronic ground state is found, which is attributed to molecule formation by femtosecond photoassociation followed by spontaneous decay. In a subsequent article [A. Merli *et al.*, submitted] quantum mechanical calculations are presented, which compare well with the experimental data and reveal further details about the observed coherent transient dynamics.

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I. INTRODUCTION

Since the first proposal of light-induced formation of ultracold molecules by Thorsheim *et al.* [1] and its experimental realization by Lett *et al.* [2], a rapidly progressing field has developed for the creation and manipulation of ultracold molecular gases by photoassociation [3, 4] and magnetoassociation using Feshbach resonances [5, 6]. On the way to lowest energies in both the external and internal degrees of freedom, numerous techniques have been developed to produce large samples of molecular quantum gases in their absolute ground state. There is, for example, the coherent de-excitation of magneto-associated molecules [7] in a STIRAP scheme or the exploitation of electronic couplings in order to transfer photoassociated molecules deeply into the singlet ground state potential [8]. Recent milestones were the observation of molecular condensates [5] or the formation of ultracold molecules in the $v=0$ internal ground state [8, 9, 10, 11].

Although these methods have enjoyed recent success, it is still a standing question as to how far coherent con-

trol of laser pulses can be applied to form molecules and control their internal states. The use of laser pulses, as opposed to cw light, has, in principle, several advantageous properties. A laser pulse has a large bandwidth, enabling excitation of atom pairs to bound molecular states resonantly over a large range of internuclear distances. Calculations show that even simple chirping of such an excitation pulse can have a large effect on the dynamics [12]. Theoretically, a second short laser pulse (shorter than the vibrational dynamics of the excited molecule) can take advantage of the vibrational wavepacket dynamics resulting from such a broadband excitation and efficiently stimulate the photoassociated molecules into stable bound ground states [13]. Furthermore, by (amplitude and/or phase) shaping both the excitation and de-excitation pulses, the excited state wavepacket dynamics can be altered to selectively populate ground state vibrational levels [14] and increase overall efficiency using learning algorithms [15].

Although such schemes might offer many advantages theoretically, the experimental implementation of them has proven to be more complicated. The use of chirped picosecond-length pulses for photoassociation to excited states has shown some promise [16] and a clear flux enhancement signal was observed. However it is not clear how far coherent control can be applied to such weakly bound wavepackets, since they theoretically have a round-trip time of nanoseconds - comparable to the spontaneous decay lifetime of the excited state (a decoherent process) and also dephase rapidly due to potential anharmonicity. Chirped nanosecond pulses have been investigated and found to alter ultracold atomic col-

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lision rates [17]. In the femtosecond regime ultracold molecule dissociation and optimization of the dissociation by shaped pulses has been experimentally verified [18, 19]. These experiments highlight that additional processes occur in the molecule-pulse interaction, which counteract the PA process. Finding the right conditions under which a photoassociation scheme becomes possible is the focus of ongoing research and indeed also of this paper.

Other recent experiments have successfully used shaped femtosecond pulses to control the photoassociative ionization of ultracold Rb atoms in conjunction with cw fields [20] and multi-photon resonant ionization of ultracold ground state Rb_2 molecules [21]. While molecular dynamics are involved in both cases, neither of these experiments have shown the existence of excited state photoassociated molecules which are suitable for coherent stabilization. Coherent dynamics in the excitation of atoms by ultrashort pulses was demonstrated in [22], which shows that electronic coherences can be created and detected using ultrashort pulses. These may also be observable on vibrational timescales (typically tens of picoseconds) when using ultrashort pulses to photoassociate atoms.

In a recent paper [23] we showed that photoassociation with shaped pulses is possible, and that coherent dynamics is visible. The purpose of the experiments was to investigate two points: The first was to answer the question of whether it is possible to photoassociate atoms to bound excited molecular states using shaped ultrashort pulses. This process is the bottle-neck in the transition from an atomic to molecular ultracold gas. The second was to observe and manipulate the coherent dynamics of the electronically excited photoassociated molecules. With the dynamics known, future experiments can be considered making use of this in conjunction with a de-excitation pulse to stabilize the molecules. In the current paper we give a detailed description of the experiment and present the analysis of the results of Ref. [23]. The comparison with the theoretical description will be presented in our subsequent article [24].

The paper is laid out as follows: In section II we discuss the general considerations one must be aware of before attempting a pulsed photoassociation experiment on an ultracold sample. In section III the experimental implementation is described. In section IV we discuss processes which compete with pulsed photoassociation. In section V the results of our experiments are presented and we show that pulsed photoassociation has occurred with coherent dynamics.

II. GENERAL CONSIDERATIONS

Although many proposals have been published which discuss ways of using ultrashort laser pulses for the efficient production of molecules from an ultracold gas, the actual implementation is restricted by a number of ex-

perimental limitations: The bandwidth and pulse shaping resolution of the available laser system, the extra potential curves present in real molecular systems (theoretically couplings between only two or three molecular potentials are considered), the trapping and cooling process applied to the atoms themselves and the influence of this on PA, and the detection of any molecules produced.

Ideally, one would select a photoassociation pulse with suitable bandwidth and tune its center frequency such that the total spectral intensity of the pulse is distributed slightly below an excited state potential asymptote, where the Franck-Condon factors (FCFs) are large. Using picosecond laser pulses (as e.g. proposed by Koch *et al.* [25]), which have a spectral bandwidth of typically tens of wavenumbers, a suitable Condon point for free-bound excitation of Rb lies at around 60 bohr radii. Around this internuclear distance FCFs are large enough to expect a reasonable photoassociation efficiency. Unfortunately, for the present experiments a tunable source of picosecond laser pulses was not available. Instead a femtosecond source was used, with a correspondingly larger bandwidth.

In addition to photoassociating the atoms, we seek to manipulate the free-bound excitation with optimally tailored laser pulses, as proposed e.g. in [14]. Ultra-short pulse shaping techniques are based on dispersive optics, such as double grating pulse shapers, which, to date, are not available with suitable resolution for narrow bandwidth picosecond pulses, and hence rules out their use. However, the manipulation of femtosecond pulses is a standard technique and offers a lot of freedom in controlling phase, amplitude and polarization [26].

For photoassociation experiments with femtosecond pulses, the large bandwidth of several hundred wavenumbers requires further consideration. The restriction of spectral intensity to below the potential asymptote is important in these experiments: Frequency components on resonance with atomic D1 (12578cm^{-1}) and D2 (12816cm^{-1}) transitions cause intolerable losses of atoms from the trap due to light scattering forces and ionization as discussed in [18]. Frequency components blue to atomic resonances can address anti-binding potential branches leading to radiation shielding effects which are known to interfere with cw photoassociation. All these effects lead to a strong reduction in atomic density within the laser overlap, which will inhibit successful photoassociation.

There are two ways to limit the spectral intensity at and above the dissociation limit: Detune the central frequency of the pulse far enough away from the dissociation limit such that the spectral intensity above the dissociation limit is low enough *or* spectrally shape the pulse to eliminate these frequencies. The first method requires detuning the pulse on the order of 200cm^{-1} (for our available laser source). The disadvantage of this method is that, although it does successfully reduce the mentioned detrimental effects, the free-bound FCFs are very low for such large detunings (by about two orders of magnitude

compared with those obtainable by using a suitable picosecond pulse tuned closer to the dissociation limit). In fact, the FCFs are only reasonable as one approaches the dissociation limit, where the spectral intensity of such a detuned pulse is unfortunately very low, resulting in a poor overall photoassociation rate. However, the second method, spectrally shaping the pulse, results in high spectral intensity close to the dissociation limit, where the free-bound FCFs are large (how close one can get to the dissociation limit depends on the shaping resolution), and therefore a good photoassociation rate. This method also very effectively reduces the mentioned detrimental processes. The photoassociation pulse central frequency, therefore, need only be tuned a few tens of wavenumbers below the molecular dissociation limit (the atomic D1 or D2 transition in our case). Spectral intensity at the potential asymptote and above can be filtered out from the pulse spectrum by an appropriate spectral amplitude transfer function, such as a step or top-hat function with the sharp spectral cut-off closely below the atomic resonance - i.e. a spectral low-pass or band-pass filter. The inset of figure 1 shows a schematic of suitable resulting pulses for photoassociation below the D1 or D2 asymptote.

The next task is the detection of femtosecond photoassociated molecules. The most reliable detection scheme is to ionize molecules from the excited state directly after their formation by the pump laser pulse. This allows the direct investigation of the molecule formation with sub-picosecond resolution immediately after the free-bound transition, thereby suppressing further interactions, for example with trapping light. The ionization is done by a second femtosecond probe pulse which is tuned to excite molecules from their first excited to the molecular ionic state (see figure 1). In such a pump-probe configuration, photoassociation and ionization laser pulses are separated in time by a defined, variable delay. Any ions produced can be mass-filtered to remove the atomic ions produced by the lasers and thus selectively view only molecular dynamics. For so-called pump-dump experiments [14, 27], which aim to coherently populate the molecular electronic ground state, this pump-probe scheme may further give important information on nuclear wave-packet dynamics in the excited state potential after femtosecond photoassociation.

III. EXPERIMENTAL PROCEDURE

The experiments were carried out in a collaboration project between the Freie Universität Berlin and the Universität Freiburg. The joint experimental setup (figure 2) consists of a femtosecond laser system with a pulse shaper, situated at the Institut für Experimentalphysik at the FU Berlin, and a transportable high density magneto-optical trap for rubidium atoms (a dark-SPOT).

The femtosecond laser pulses were produced by a Coherent Mira oscillator and amplified by a Coherent RegA

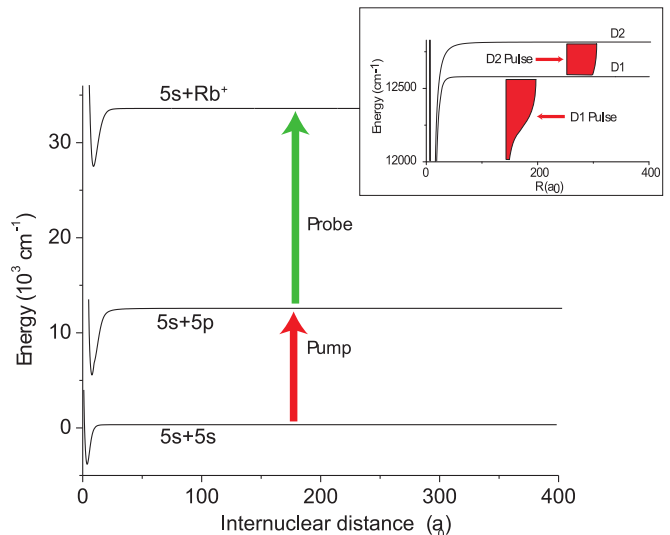


FIG. 1: (color online) Scheme of pump-probe photoassociation. Formation of molecules in an excited state by exciting a pair of colliding ultracold atoms with a shaped pump-pulse. Transfer to molecular ion by a time-delayed probe-pulse. Inset: Pulse spectra used when exciting to potentials with D1 (D1 pulse) and D2 (D2 pulse) asymptotes.

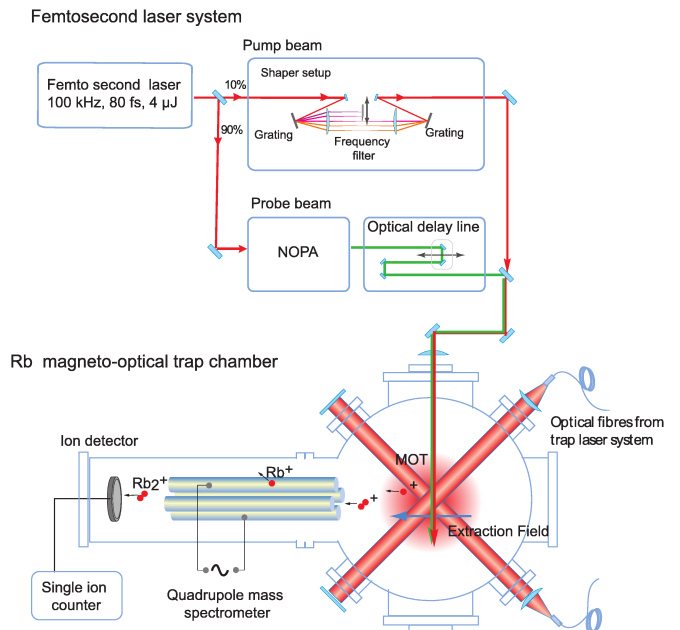


FIG. 2: (color online) Experimental setup for pump-probe photoassociation. Femtosecond pump pulses pass a zero dispersion grating pulse shaper, realizing an optical low pass to filter atomic resonances. Probe pulses are created by frequency conversion in a NOPA (non-collinear optical parametric amplifier) and pass a controllable optical delay stage. Pump and probe beams are spatially overlapped and focused into a rubidium dark-SPOT. Molecular ions created in the trap are mass selected by a radio frequency mass analyzer.

9050, yielding pulses of $4\mu J$ energy and an autocorrelation of 80 fs FWHM at 100 kHz repetition rate. Output pulses have a spectral width of 390 cm^{-1} FWHM and are either centered around 12500 cm^{-1} (800 nm), which is 78 cm^{-1} below the dissociation limit of the first electronically excited $5s+5p_{1/2}$ states, or centered around 12739 cm^{-1} (785 nm), which is 78 cm^{-1} below the dissociation limit of the electronically excited $5s+5p_{3/2}$ states.

10% of the laser output is split off and used for the pump pulses. The pump pulses pass through a zero dispersion, double grating pulse shaper equipped with a spatial light modulator (CRI, SLM 640) to manipulate spectral phases and amplitudes with a spectral resolution of 2.2 cm^{-1} . Using the SLM for attenuation of spectral components on resonance with rubidium transitions proved to be insufficient as the 2% residual transmission still causes significant atom loss from the magneto-optical trap. The spectral low pass filter was, instead, realized by placing an additional physical block in the shaper's Fourier plane, spatially blocking the path taken through the shaper by the high frequency part of the pulse spectrum. This block consists simply of a razor edge (see figure 2) which is mounted on a precision stage. This setup provides a high-attenuation optical low-pass filter with a sharp and adjustable cut-off frequency.

In order to adjust the cut-off of the filter to a suitable frequency we need to know: First what the position versus frequency conversion of the precision stage is, and, second, at what position reading of our high precision stage the atomic resonance frequency is situated. The answer to the former is given by the zero dispersion shaper's properties (grating frequency and lens focal length), whereas the answer to the latter is best measured experimentally. The fluorescence of rubidium atoms in the magneto-optical dark spot trap was measured on a photodiode as the cut-off was scanned. The laser beam was chopped (to minimize error due to atom-loss and trap fluctuations) and then passed through the center of the cold cloud. As soon as the spectral filter transmits an atomic resonance frequency, the relative trap fluorescence (with vs. without beam) increases. The resulting data has a step-like characteristic at the resonance which is fitted by an error function to retrieve the resonance position in the Fourier plane with a precision of about $86\mu\text{m}$, corresponding to a frequency resolution of 1.8 cm^{-1} .

Ionization probe-pulses are produced by frequency conversion of the RegA output in a non-collinear optical parametric amplifier (NOPA) [28] which uses the remaining 90% of the RegA output power. The probe-pulses are centered at 20160 cm^{-1} (496 nm) when using a D1 pulse and 19802 cm^{-1} (505 nm) when using a D2 pulse, have a spectral FWHM of 1000 cm^{-1} (25 nm), pulse energies of up to 50 nJ and non-transform-limited autocorrelation durations of about 600 fs FWHM. To vary the pump-probe delay the probe pulses pass an optical delay stage (PI, M-531). During the pump-probe scans the delay is typically scanned with a speed equivalent to a delay change of 15 fs/s.

Before entering the vacuum chamber of the magneto-optical trap, both beams are spatially overlapped using a dichroic mirror and focused into the trap to waists of $\approx 120\mu\text{m}$ and $\approx 100\mu\text{m}$, resulting in typical peak intensities of $2.5 \times 10^4\text{ MW/cm}^2$ for the pump and $1.4 \times 10^3\text{ MW/cm}^2$ for the probe pulses.

The magneto-optical dark SPOT [29, 30, 31] captures 10^8 ^{85}Rb atoms at densities of 10^{11} cm^{-3} and temperatures of $100\mu\text{K}$. Trap densities and sizes are measured by absorption imaging, the trap fluorescence is continuously monitored by a photodiode. Trapping light is produced by two single-mode diode lasers which are actively stabilized to frequency modulation spectroscopy signals [32]. The trapping laser is detuned by 3Γ (18 MHz) from the $F=3 \rightarrow F'=4$ transition and reaches a peak intensity of 18 mW/cm^2 . The second laser is stabilized to the $F=2 \rightarrow F'=3$ transition for repumping.

The key parameter of a dark SPOT is the steady state ratio of upper to lower hyperfine ground state population of the trapped atoms ($p = N_{\text{res}}/N_{\text{total}}$), where N_{res} is the number of atoms in a state near resonance with the trapping light and N_{total} is the total number of atoms. In ^{85}Rb the relevant levels are the $F=2$ and $F=3$ hyperfine ground states, which are split by 3.1 GHz. For the dark SPOT configuration, repump laser intensity is removed at the position of the trap by means of two crossed, hollow beams of repump light. This allows optical pumping of population from the upper to the lower hyperfine ground state via off-resonant excitation from the $F=3$ electronic ground state to the $F'=3$ electronically excited state by the trapping laser in this region. The effect of residual repump light in the hollow beam overlap is reduced by detuning the laser by 30 MHz red to the $F=2 \rightarrow F'=3$ transition. Atoms can be optically pumped between the hyperfine states by two additional laser beams which fill the trap center only. A depumper on resonance with the $F=3 \rightarrow F'=2$ transition decreases the $F=3$ population and a separate beam of repump light increases it. In order to measure the relative populations in both hyperfine states, all trapped atoms are pumped to the upper $F=3$ state by a 50 ms pulse of the repump fill beam, resulting in a flash of fluorescence which is detected by the photodiode [30]. The population ratio p is then deduced from the fluorescence signals in the dark- and repumped trap, assuming that the trap fluorescence is proportional to the $F=3$ population and the fluorescence is dominated by decay from the $F'=4$ excited state. In our setup, the detuning of the repumper by 30 MHz alone causes 90% of the atoms to be kept in the lower $F=2$ hyperfine state (without the additional depumper beam), which provides the highest densities and therefore optimal conditions for photoassociation experiments. In our experiments we vary the parameter p to exclude competing processes such as photoassociation by trapping light (see sec. IV).

Atomic and molecular ions produced in the trap are extracted by an electric field of 40 V/cm and detected by a channeltron. Before the channeltron a radio fre-

quency (rf) quadrupole filters the incoming ions according to their mass (see figure 2). Alternatively we can operate the mass selection as a time-of-flight spectrometer. Electronic ion signals are high pass filtered to remove any residual rf signal from the mass filter before they are amplified and digitized by a constant fraction discriminator. Digital pulses are acquired by a fast counter and integrated over 100 ms. The dark count rate (without lasers and trapped atoms) of the ion detection system is 0.1 Hz. During pump-probe scans the ion count rate, trap fluorescence and the actual pump-probe delay are gathered by the data acquisition computer.

Despite blocking the atomic resonances, the femtosecond pulses produce large numbers of atomic ions by off-resonant pump-probe excitation. Without mass filtering by the rf quadrupole, these would totally saturate the detection system and prohibit the identification of small numbers of molecular ions. Mass spectra of the pump-probe created ions in the trap, using the rf quadrupole, show two peaks at the atomic ^{85}Rb and the molecular $^{85}\text{Rb}_2$ masses with resolutions of 4 amu. For different mass settings only the system's dark count rate is detected. This shows that ion signals measured on the $^{85}\text{Rb}_2$ mass represent exclusively rubidium molecular ions and no background due to different charge states or ion species has to be considered.

IV. COMPETING PROCESSES

The identification of femtosecond photoassociation relies very strongly on understanding alternative sources of the molecular ion signals detected during the experiments. Two potential alternative pathways exist for producing Rb_2^+ ions - a) excitation of trap-light-produced molecules and b) collisional autoionization via Rydberg states.

Photoassociation of rubidium dimers can occur due to trap light [33]. These molecules may be ionized by the femtosecond pulses from the electronic ground- (the pump pulse + the probe pulse) or excited- (the probe pulse only) state. In a dark SPOT the efficiency of trap light photoassociation depends on the atomic population of hyperfine ground states. This distribution can be characterized by the ratio, p , of atoms in the upper $F=3$ state, which participate in the trapping cycle, to the total number of atoms. The density of atoms varies over about one order of magnitude as p changes and reaches its maximum around $p = 0.1$ [30]. As p is varied, the photoassociation rate for both femtosecond and trap light PA changes due to its dependence on the density squared. Because of the tight bandwidth of the trapping lasers, photoassociation by trap light is additionally sensitive to the hyperfine configuration of the colliding pairs [34], which is directly influenced by p , whereas the broadband femtosecond pulses are not. The examination of molecular ion rates under variation of the atomic hyperfine ground state populations is a good measure to distinguish

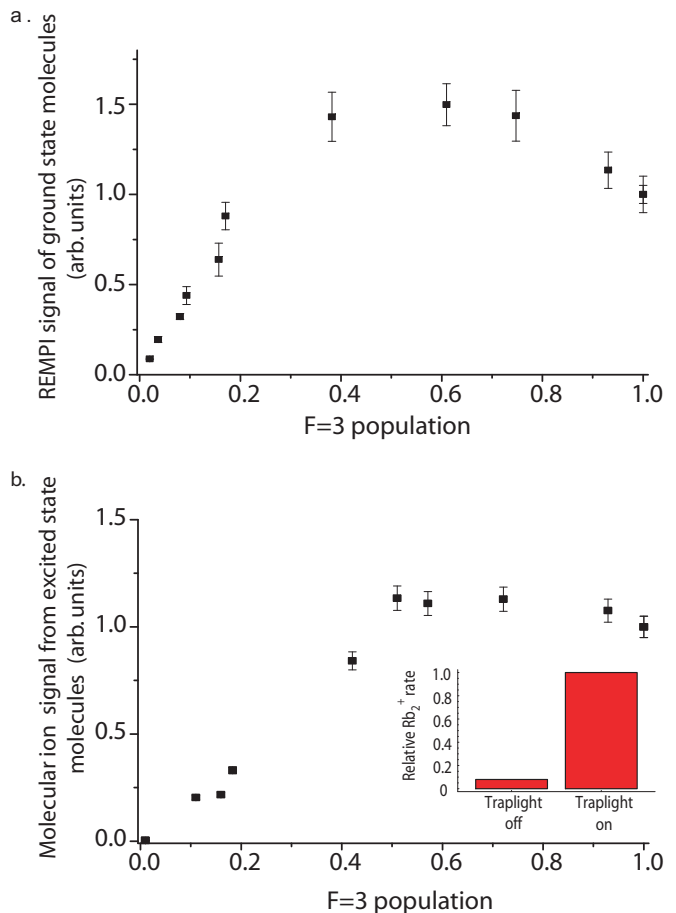


FIG. 3: a. Molecules photoassociated by trapping light, ionized from $5s+5s$ ground state by nanosecond dye laser pulses. b. Molecules produced by trapping light, ionized from the $5s+5p_{3/2}$ excited state by femtosecond probe pulses. Inset: Relative Rb_2^+ rate with and without trapping light present simultaneously with the femtosecond pulses for $p = 0.01$.

trap-light-formed and femtosecond-formed molecules.

The trapping laser photoassociates atom pairs to states below the $5s+5p_{3/2}$ potential asymptote. After a lifetime of 12 ns they spontaneously decay to their electronic ground state, thereby populating the uppermost vibrational levels of the $^3\Sigma_u^+$ $5s+5s$ metastable state [33, 35]. The contributions of the excited state trap-light-formed molecules (1 probe photon) and the ground state trap-light-formed molecules (1 pump + 1 probe photon) to the molecular ion signal are investigated separately.

For an independent measurement of the dependence of trap-light-formed ground state molecules on the $F=3$ population, we use resonant two-photon excitation (REMPI) for state selective detection [35]. A Nd:YAG pumped dye laser, operated at 602 nm with 10 mJ pulse energy and a 10 Hz repetition rate, is focused into the trap. The detected molecular ion rates were on the order of 0.5 per pulse for a trap with 100% $F=3$ population ($p = 1$). The formation of ground state molecules as a

function of p is shown in figure 3a. The molecular signal is low at small p , reaches its maximum at about $p = 0.6$ and drops again for $p = 1$. The trap density has a very different p dependence, and peaks around $p = 0.1$ [30]. Thus the comparatively slow rise in figure 3a to $p = 0.6$ can be attributed to a photoassociation process that requires at least one of the colliding atoms to be in the $F=3$ hyperfine state.

A similar p dependence is observed for the molecular ion signal which is detected when only the femtosecond probe pulses interact with the trap (figure 3b). This signal rises to reach a maximum at around $p = 0.5$ and drops again as p approaches unity. The rate of molecular ions which are detected this way is up to 500 Hz.

By shuttering both the trapping light and the femtosecond probe beam it is possible to determine the origin of these ions. In one case the femtosecond probe-pulses were incident on the MOT only when the trap light was shuttered off (the trapping light had a large on/off duty cycle in order to avoid density loss). In the other case, the timing of the shuttering of the femtosecond probe-pulses was shifted so that they were incident on the MOT when the trap light was on (the trap light had the same duty cycle as the first case in order to have comparable conditions). The ion signal is strongly correlated to the presence of trapping light, as shown in the inset of figure 3b for the two shuttering schemes. If the trapping lasers are off when the probe-pulses hit the trap, the Rb_2^+ signal is only around 10% as large as if the trapping lasers are on when the probe-pulses hit the trap. The reason for this is that as soon as the trapping lasers are shuttered off, no more molecules can be photoassociated to the excited state and the excited state molecules present at that time decay with a spontaneous lifetime of 12 ns. After this decay time there are no molecules in the excited state until the trap light is shuttered on again. The strong reduction in molecular signal observed when the molecules are in the ground state shows that the probe pulses can ionize molecules from the excited $5s+5p$ state, but not from the ground state. We therefore attribute the signal from figure 3b to molecules which are photoassociated by trapping light into the $5s+5p_{3/2}$ potential and which are then ionized by the femtosecond probe pulses. This explains the similarity of the p dependence found in figures 3a and b, as the $5s+5p_{3/2}$ population represents the intermediate step in the formation process of ground state molecules by trapping light. In the pump-probe experiments the trapping light was *not* shuttered, and therefore there was a steady-state population of trap-light-photoassociated molecules, which are also ionized by the probe laser and detected, causing a background molecular ion signal. This background is measured separately and may be corrected for.

The second process that can lead to the formation of molecular ions is the associative autoionization in collisions of Rydberg and ground state atoms [36]. Rydberg atoms are created from ground state atoms by excitation with a pump and a probe pulse. The resulting dis-

tribution of Rydberg states peaks at principal quantum number of $n=12$. Collisional associative ionization (CAI) may occur during the spontaneous lifetime of the Rydberg state, following the reaction: $\text{Rb}(nl) + \text{Rb}(5s) \rightarrow \text{Rb}_2^+ + e^-$. The contribution of this process to the observed molecular ion rate can be estimated from a capture model [37]. The required C_6 coefficients were calculated following [38], where the necessary ground state wave functions were obtained using a model potential described in [39]. In combination with the trap temperature of $100 \mu\text{K}$, we estimate a rate coefficient for associative ionization of $k = 4 \cdot 10^{-10} \text{ cm}^3/\text{s}$. An upper limit on the CAI rate can be estimated by attributing the total atomic trap loss rate at positive pump-probe delays to the excitation to Rydberg states. In reality, trap-loss involves many processes (for example atomic ionization) and so the actual rate is most certainly lower than this. With the measured atomic density of 10^{11} cm^{-3} and an average lifetime of the addressed Rydberg levels of $1.5 \mu\text{s}$ [40] we estimate the maximum contribution of this process to be less than 20% of the molecular ion signal detected in the pump-probe experiments. Furthermore, this process can only occur at positive delays (pump before probe) when the first step in the Rydberg excitation proceeds via the pump pulse. At negative delays, where significant numbers of molecular ions are also detected (see section VC), the Rydberg excitation would have to proceed via an initial excitation by the probe pulses, however no appropriate atomic transitions are available for such a process.

V. FEMTOSECOND PHOTOASSOCIATION

A. Pump-probe spectra

Figure 4 shows measured molecular ion count rates as a function of the delay between a pump-pulse tuned below the D1 asymptote (see “D1 pulse” inset figure 1) and an ionization probe-pulse. Going from top to bottom, the spectral cut-off frequency, relative to the D1 transition frequency (the cut-off detuning), decreases from -12 cm^{-1} to -6 cm^{-1} (the minus sign means red to the D1 transition) in steps of 2 cm^{-1} . The data were smoothed by averaging over 10 adjacent points. The dashed lines indicate an estimate of the background ion rate caused by probe laser ionization of trap-light photoassociated molecules (see section IV). In this particular set of measurements the background level was not measured, rather estimated by extrapolating the power-dependence of the ratio of the negative-delay level to the measured background level of a previously-measured data set.

The data show that the detected molecular ion rate clearly depends on both the pulse delay and the pump pulse’s spectral cut-off frequency. The general form of the curves is the following: For negative delays (when the ionization probe-pulse precedes the pump pulse) we observe a constant rate of molecular ions. At $t=0$ both pulses

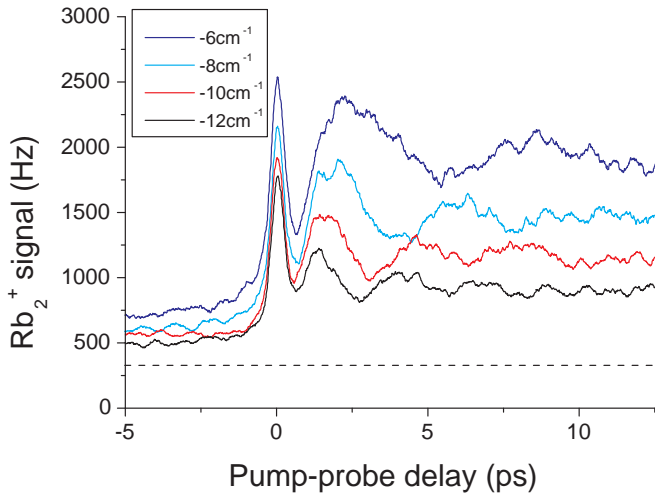


FIG. 4: (color online) Dynamics of Rb_2^+ signal with a D1 excitation pulse. Pump-probe data for cut-off detunings of -6 cm^{-1} to -12 cm^{-1} from the D1 asymptote. The dashed line indicates the background level (see text).

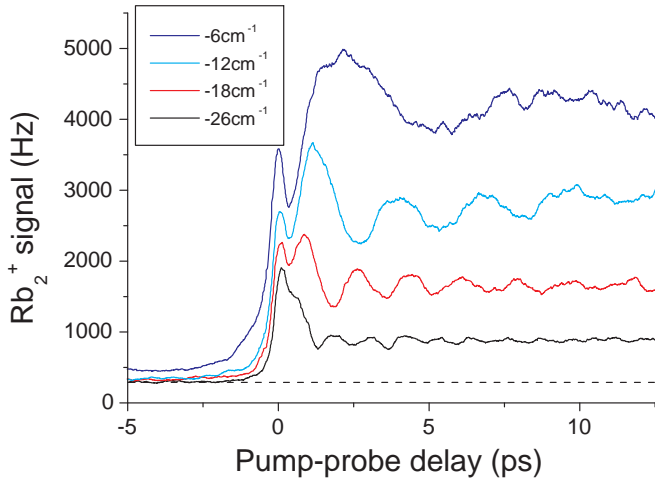


FIG. 5: (color online) Dynamics of Rb_2^+ signal with D2 excitation pulse. Pump-probe data for cut-off detunings of -6 cm^{-1} to -26 cm^{-1} from the D2 asymptote. The dashed line indicates the background level (see text).

coincide in time and the count rate increases drastically, forming a peak of 0.5 ps width. For positive delays, a clear increase in the molecular ion signal, compared to negative delays, is observed. Additionally, the signal is modulated by characteristic oscillations with periods of a few picoseconds, which are fully damped after a short time. As the cut-off detuning is decreased (going from top to bottom in figure 4) the molecular ion signal also increases for all delays, as does the modulation period for $t > 0$. Significant pump-probe signals are only observed in the experiments for cut-off detunings of less than -30 cm^{-1} .

Figure 5 shows the corresponding results with the “D2 pump-pulse” (see inset figure 1) and an ionization probe-pulse. Except for the overall count rate, quantitatively identical data are obtained on the D2 asymptote as are obtained on the D1 asymptote. For experiments on the D2 asymptote, the frequencies red to and including the D1 resonance frequency were additionally blocked as shown in the inset of figure 1. This second cut-off frequency was typically 20 cm^{-1} blue to the D1 atomic resonance. Interestingly, this suggests that the dynamics of our process is not sensitively dependent on the form of the addressed potential. The background level was estimated to be similar to the negative-delay level for the -26 cm^{-1} data set.

With our setup one might expect to observe the propagation of a nuclear wave-packet (which is created by the pump pulse and subsequently oscillates in the excited state potential well) under the assumptions that a) a well-localized wave-packet is created, b) the dephasing of the wave-packet is not rapid and c) one looks on the appropriate time-scale. The ionization pulse would result in a delay-dependent molecular ion signal due to motion on the internuclear degree of freedom. Based on the spectral components of our pump-pulse and with knowledge of all the potentials corresponding to this asymptote, we expect the nuclear oscillation time to be on the order of tens of picoseconds, rather than the few picoseconds we observe. Even pump-probe scans over longer delay ranges do not show oscillations on the expected time-scales. Since the observed oscillations are therefore not consistent with a vibrational wave-packet, other processes must be considered in order to explain the observed signals.

To get quantitative information for further analysis we extract characteristic parameters from the data. In order to obtain the mean value of molecular ion counts for negative delays, we take an average of data points for $t < -3 \text{ ps}$. The modulation periods at positive delays are extracted by fitting a damped oscillatory function to the data, with a steady-state asymptotic level, a modulation amplitude, a damping time and an oscillation period and phase relative to $t=0$. An additional linear slope parameter accounts for a slow linear variation in the detection rate caused by a slow systematic drift in the apparatus during the scan.

A correlation plot (see figure 6) of the fitted modulation frequencies shows that the modulation frequency matches the cut-off detuning. This behavior is not expected for a vibrational wave-packet oscillating in an anharmonic molecular potential. The observed oscillatory dynamics are instead due to so-called coherent transients [22, 23], which is a coherent energy exchange between molecules and the pump-pulse laser field. A detailed discussion of this is given in our accompanying theoretical paper [24].

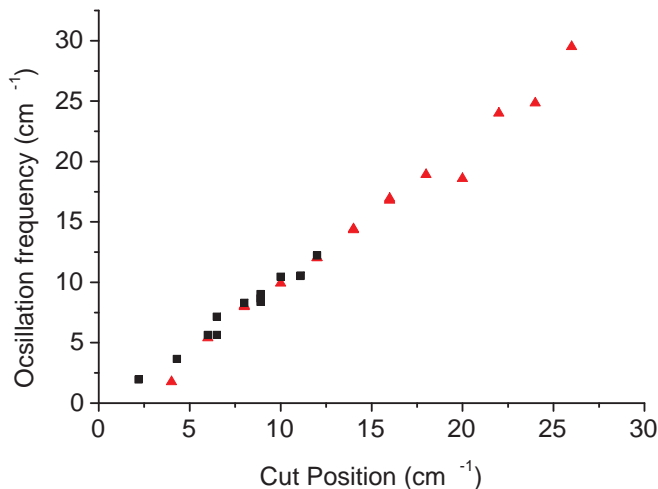


FIG. 6: (color online) Frequencies of modulations on pump-probe ion signals at $t > 0$ versus cutoff position for both D1 (black squares) and D2 (red triangles) pulses.

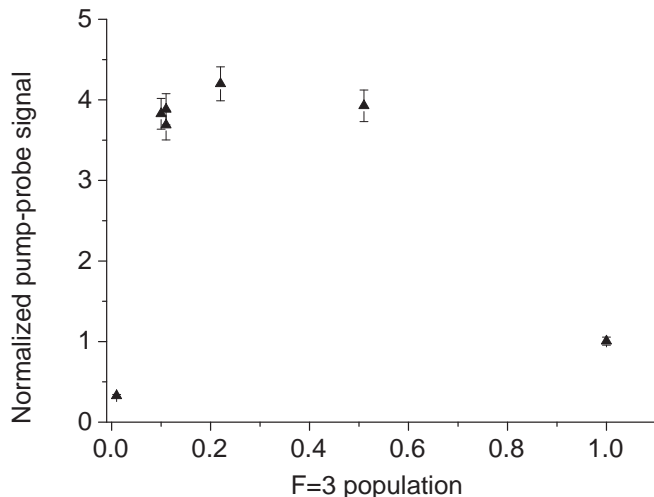


FIG. 7: (color online) Pump-probe mean molecular ion signal at $t \gg 0$ as function of dark SPOT F=3 population for D1 pulse. A similar curve is obtained for the D2 pulse.

B. Asymptotic behavior

In order to confirm that the pump-probe molecular ion signal at positive delays originates from the excitation of free atom pairs by the femtosecond laser and not from trap-light photoassociated ground state molecules, we performed pump-probe scans at different configurations of the dark SPOT - i.e. different values of the parameter p . These measurements can be compared to those found in section IV (figure 3).

Figure 7 shows the dependency of the asymptotic molecular ion signals ($t \gg 0$) as a function of p . The signal shows a steep increase from $p = 0$, reaches its

maximum at about $p = 0.2$ and drops for p approaching unity. This curve looks very similar to the atomic density curve in a dark SPOT [30] and so the pump-probe signals only seem to be sensitive to the change in density as p rises and not the population in the F=3 state - consistent with photoassociation from the femtosecond laser. This can be contrasted with the measurements shown in figure 3, showing photoassociation by trap light, where the much slower rise for small p indicates a process which requires at least one of the colliding atoms to be in the F=3 state.

We therefore conclude that the molecular ion signals from the pump-probe scans must predominantly originate from the photoassociation of colliding atom pairs by the femtosecond pump pulses. In light of this, the pump-probe data presented in this work were taken at $p = 0.1$ where we measured highest trap densities and trap light photoassociation rates are low, according to figure 3 a, so that their contribution is, if present, of minor importance.

Figure 8a. shows the variation of the asymptotic pump-probe signals with the spectral cut-off detuning. A clear increase in the Rb_2^+ rate is observed as the cut-off approaches the potential asymptote. As discussed previously, the signal at $t > 0$ represents the population in the $5s+5p$ manifold. For smaller cut-off detunings, the coupling of the electronic states by the pump pulse increases, resulting in a higher excitation efficiency. In the pump-probe scans, since the excited state population is larger, the detected ion rate will be correspondingly higher.

Figure 8b. shows the variation of the asymptotic Rb_2^+ rates as a function of pump-pulse energy. The signals rise non-linearly with the pump-pulse energy. Although only the asymptotic values ($\Delta t \gg 0$) have been shown, the signal gets larger for all delays, as the pump-pulse energy is increased. This power dependence indicates a non-linear character of the pulsed PA process.

Figure 9a. shows the result of pump-probe scans using a D2 pulse with a cut-off of -14cm^{-1} as the NOPA center frequency is changed. The temporal broadening for red detuned probe pulses, particularly visible for the peak at zero delay, can be explained by the increased duration of the probe-pulse for higher center wavelengths. Figure 9b shows the steady-state levels at $t \gg 0$ using D1 pump-pulse and a D2 pump-pulse as the NOPA center frequency is changed. Clearly, the molecular ion rate drops as the center frequency is moved further away from the dissociation limit (vertical lines) for both the D1 and D2 pulses, which supports the 1+1 REMPI scheme. With a D2 pulse, the signal begins to increase at a NOPA central frequency of around 18750cm^{-1} , 2124cm^{-1} away from the dissociation limit, which is 20874cm^{-1} above the $5p_{3/2}$ level. With a D1 pulse, the signal begins to increase at a NOPA central frequency of around 19800cm^{-1} , 1312cm^{-1} away from the dissociation limit, which is 21112cm^{-1} above the $5p_{1/2}$ level. (The dissociation limit is calculated as the atomic ionization limit of 33690.81cm^{-1} minus the asymptotic energy

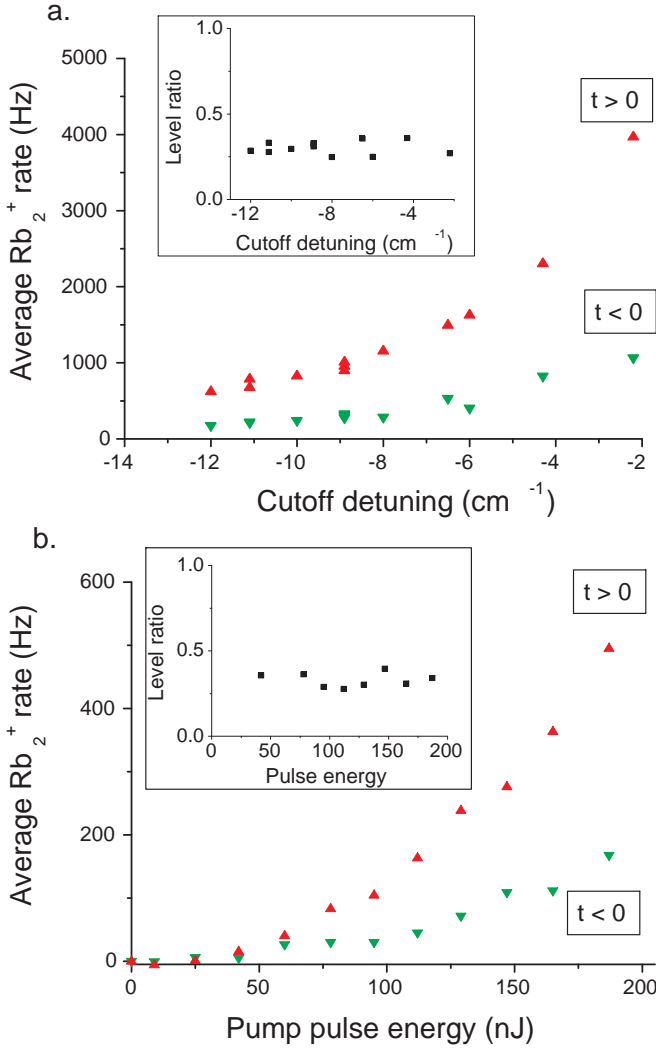


FIG. 8: a.) D1 pump-probe Rb_2^+ asymptotic rates versus spectral cutoff position. \blacktriangle : Rb_2^+ at positive delays. \blacktriangledown : Rb_2^+ at negative delays. Inset: Constant ratio of ~ 0.3 between time-averaged levels at negative and positive delays for different cutoff detunings. b.) Pump-probe Rb_2^+ average rates pump-pulse energy. \blacktriangle : Rb_2^+ at positive delays. \blacktriangledown : Rb_2^+ at negative delays. Inset: Constant ratio of ~ 0.3 between time-averaged levels at negative and positive delays for different pump-pulse energies

of the populated molecular states - i.e. $12578.950 \text{ cm}^{-1}$ for the $5p_{1/2}$ states and $12816.545 \text{ cm}^{-1}$ for the $5p_{3/2}$ states, all relative to the atomic ground $5s_{1/2}$ state energy.) The depth of the ionic potential is approximately 6000 cm^{-1} [41], so, in principle, it would be possible to populate more deeply bound levels in the ionic potential with the available laser frequencies. From our data it seems that this is not the case, rather we populate mid-to weakly-bound states in the molecular ion potential. After the photoassociation pulse we expect, due to laser spectrum and FCF considerations, to be mostly populating states within approximately a few tens of wavenum-

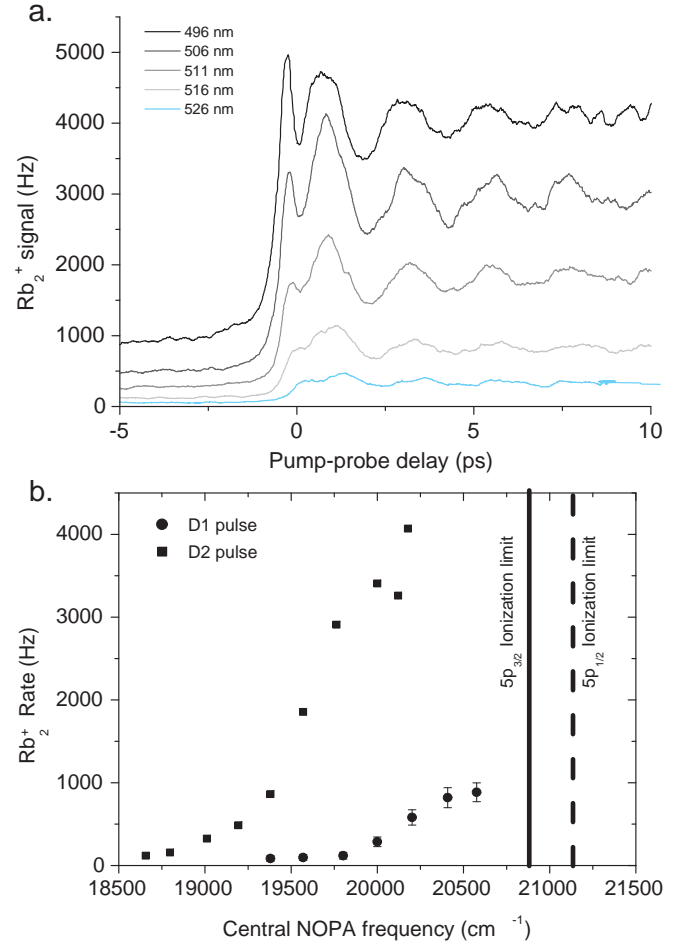


FIG. 9: a) Pump-probe scans for different center values of the NOPA (ionization) pulse using a D2 pulse. b) Rb_2^+ signal at $t \gg 0$ for different center frequencies of the NOPA pulse.

bers of the $5p_{1/2}$ or $5p_{3/2}$ dissociation limit (in fact, as will be shown in our follow-on paper, we are mainly populating levels even closer to the dissociation limit of the $5s+5p$ states.) Such weakly bound molecules will be excited most efficiently to reasonably weakly bound ionic states.

C. Signal at negative delays

Molecular ion levels at $t \gg 0$ and $t \ll 0$ show highly correlated behavior over a broad range of cut-off detunings and pump-pulse energies. The insets in figures 8 a and b show the ratios of asymptotic levels of molecular ion rates for $t \gg 0$ and $t \ll 0$ as the cut-off detuning and the pump-pulse energy is varied. This ratio is fairly constant at 0.3 for both cases. It is therefore possible that the ions detected at positive delays and negative delays have a similar origin, with just a different overall ionization efficiency. PA due to the probe-pulses is not expected to take place, due to the lack of a suitable

transition for ground state pairs and can be therefore ruled out. The signals are clearly different in that no oscillations are seen for negative delays, which suggests a possible mechanism which is consistent with the observed behavior. The molecular ions which are detected at negative delays must be first photoassociated into the $5s+5p$ state by the pump-pulse before undergoing further transitions and ending up as molecular ions. At negative delays the probe- precedes the pump-pulse, so any signal related to a $5s+5p$ excitation must be due to a previous pair of pulses. The temporal separation between pulse pairs of $10\mu s$ is much longer than the $12 ns$ spontaneous lifetime of the $5s+5p$ state. Therefore, any population in the first excited state, created by a pump pulse, will have decayed before a probe pulse of a successive pair of pulses interacts with the trap.

The ionization of residual population in the excited state can therefore be excluded as the origin of the negative delay signal. However, the negative delay signal can be attributed to molecules in the electronic ground state. These are formed by spontaneous decay from bound excited states, previously photoassociated by a pump pulse. The pump-pulse excitation results in a considerable population in bound vibrational states. Upon decay these may either dissociate or end up in bound molecular states. Vibrational ground states are populated according to their Franck-Condon overlaps with the $5s+5p$ vibrational states. As the $5s+5p$ molecules are loosely bound and of long range character, ground state molecules can also be expected to populate the uppermost vibrational states in the ground state potential. In cw-photoassociation experiments [35, 42] this process is well known and the major formation process of ultracold molecules in their electronic ground state. In our experiments, ground state molecules are detected by excitation to an intermediate state below the $5s+4d$ or $5s+6s$ asymptotes by a probe-pulse and subsequently ionized by a pump-pulse. The ratio of 0.3 between the asymptotic levels at positive and negative delays is the relative efficiency for direct pump-probe ionization versus ionization via formation of ground state molecules. The lack of oscillations on this signal is due to the long time between formation and ionization with an incoherent spontaneous emission step in between.

D. Influence of linear chirp

A topic of great interest in photoassociation by femtosecond pulses is the proposed possibility to coherently control the process by imprinting defined phases on the molecular quantum state to manipulate its temporal evolution. The application of linear chirps, for example, is expected to increase the excitation efficiency of the free bound transition in the perturbative regime [12, 43, 44, 45, 46] by adiabatic transfer. Also the nuclear dynamics can be influenced by imprinting the field's phase onto a coherent vibrational wavepacket in

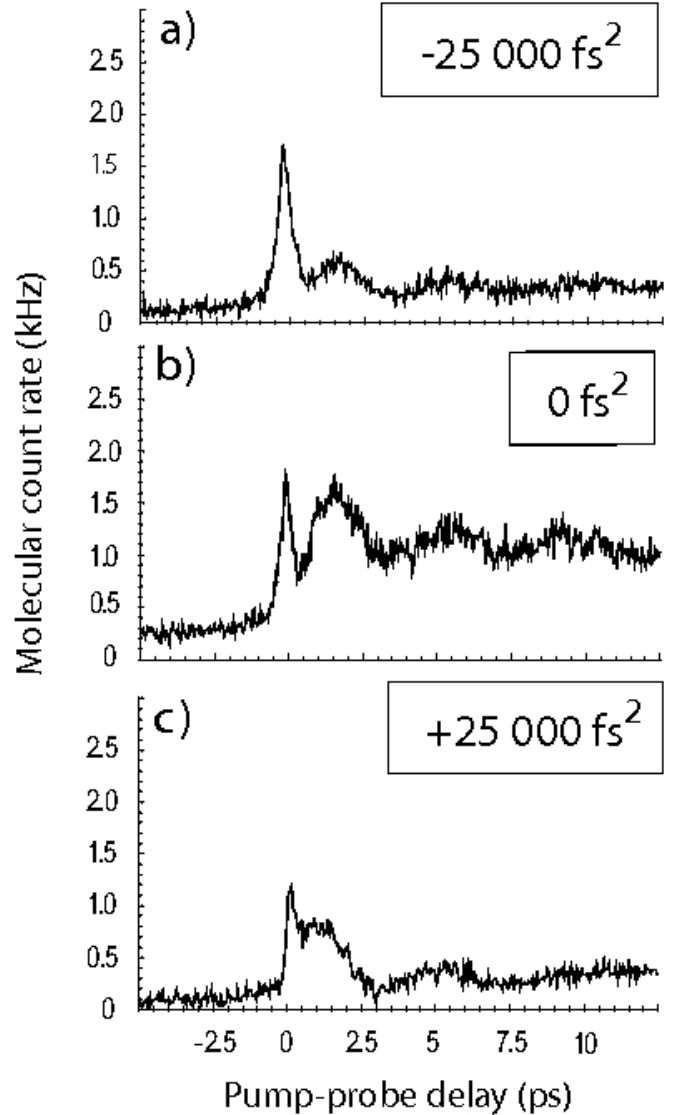


FIG. 10: Pump-probe Rb_2^+ rate for chirped and cut pulses with spectral cut-off at -8 cm^{-1} . The linear chirps are: a) -25000 fs^2 , b) no chirp and c) $+25000\text{ fs}^2$.

the excitation. As demonstrated by Koch *et al.* [27] or Poschinger *et al.* [14] this may allow optimization of the coherent formation of bound ground states in pump-dump experiments.

In our pump-probe photoassociation experiments, we are not in the perturbative regime, as can be seen from our non-linear power dependence in figure 8. Additionally our signal does not originate from nuclear wavepacket motion. Nevertheless, chirping the pump-pulses reveals interesting dynamics. We modified the pump pulse's phase by applying a quadratic spectral phase (using the SLM in the Fourier plane in addition to the knife-edge) in order to investigate the effect on the pump-probe signal.

The spectral cut-off, in combination with the quadratic phase, causes strong distortions of the pulse's ampli-

tude and frequency behavior during the pulse maximum. Compared to an unchirped pump-pulse, the maximum field strength is reduced by a factor of ~ 2 and its duration is increased to 1.2 ps FWHM. The instantaneous frequency varies strongly on a sub-picosecond timescale and only the time-averaged slope within $t = \pm 1$ ps shows the linear progression which corresponds to the quadratic phase coefficient $b_2 = \pm 25\,000 \text{ fs}^2$. The major effect of the quadratic phases on the photoassociation is a strong reduction of the excited state population (and hence the molecular ion signal). For both positive and negative chirps, the molecular ion rate drops below 25% of the zero-chirp level for $b_2 = \pm 25\,000 \text{ fs}^2$. A strong reduction in ion rate supports the argument that we are photoassociating to the $5s+5p$ asymptote outside of the perturbative regime, since non-linear processes require high peak intensities during the pulse maximum.

The spectral composition of the pulses, of course, is unaltered and clearly the dynamics are similar to the unchirped case. The modulations are observable even for large values of b_2 , decreasing only in amplitude whereas their period remains unchanged. The main difference in the dynamics is a phase-shift between the peak at $t = 0$ and the oscillations, which is chirp-dependent. This is discussed in more detail in the accompanying theoretical paper [24]. The contrast between these results and the proposed efficiency increase by chirped pulses, e.g. in [12] arises from the fact that these proposals consider resonant (within pulse spectrum) excitation to bound levels in the free-bound transitions. As discussed above this is not the case in our photoassociation experiments which mainly rely on non-linear, off-resonant excitations.

E. Fluorescence and trap loss

Similar dynamics are found for the atomic-loss in the MOT as for the photoassociation of free-atom pairs. This is detected via the variation of the trap fluorescence during the pump-probe scans, which indicates a delay-dependent loss of atoms from the trap (excitation and loss processes will be discussed shortly). As shown in figures 11 and 12 the atomic losses increase for smaller cut-off detunings and show the characteristic modulations. The results look closely related to those found in [22].

In the present experiments, the trap-loss rate at $t > 0$, due to the femtosecond lasers, is estimated to be about $4 \cdot 10^6$ atoms/s, when using a D1 pulse, which exceeds the femtosecond photoassociation signal by three orders of magnitude. Similarly to the collision pairs, single atoms are off-resonantly excited to the $5p_{1/2}$ or $5p_{3/2}$ state by a pump-pulse. Trap loss occurs by the subsequent probe-pulse excitation. The probe pulse spectrum reaches from low lying Rydberg states at $n=8$ up to the ionization threshold. Thus atoms may either be directly ionized or excited to Rydberg states, the decay of which also results in trap loss.

The modulation on the trap fluorescence shows that

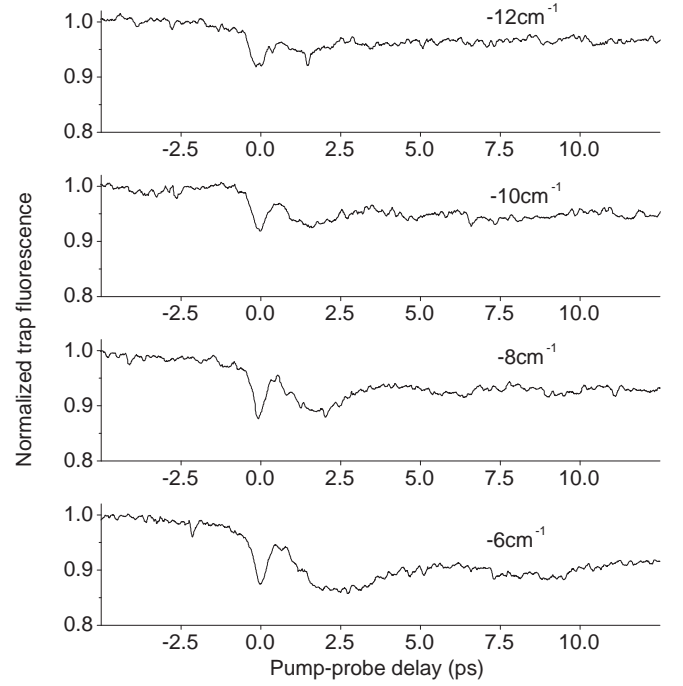


FIG. 11: Pump-Probe signals of trap fluorescence under variation of pump-probe delay using a D1 pulse.

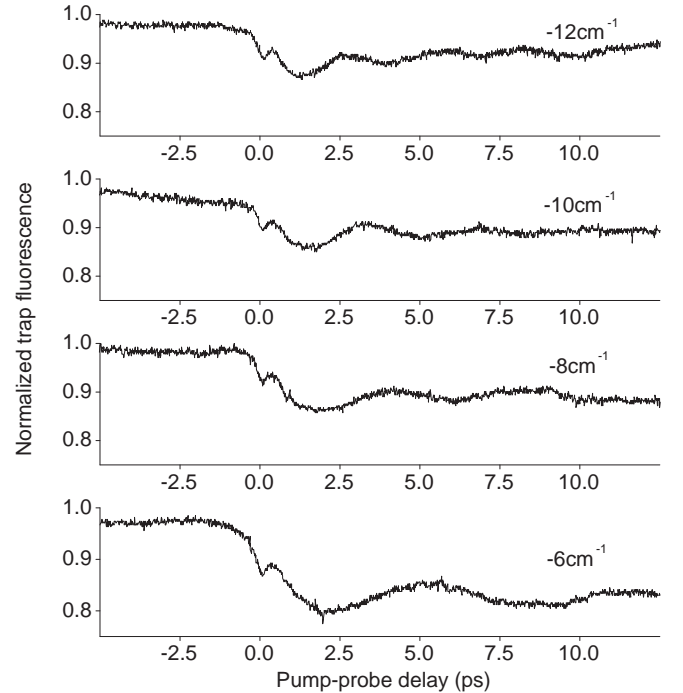


FIG. 12: Pump-Probe signals of trap fluorescence under variation of pump-probe delay using a D2 pulse.

large numbers of atoms interact with the pump pulse field, in the same manner as discussed for the photoassociated molecules. The large loss rate of atoms as compared to the molecular ion count rate shows that atomic excitation is by far the dominant process occurring in the trap during the pump-probe experiments. With this in mind, the femtosecond photoassociation discussed in the previous sections may also be regarded as the excitation of single atoms plus the interaction with a neighboring atom. Only a small fraction of atoms which have a close partner in the interaction volume can be excited to the molecular ionic state by the pair of pump-probe pulses. Due to the mass selection by the rf quadrupole, the ion detection is restricted to molecular ions and thereby selects this small fraction of close pairs in the interaction volume.

VI. CONCLUSION

In summary, we have demonstrated the photoassociation of ultracold atoms using shaped ultrashort laser pulses. The femtosecond laser mainly excites into weakly bound excited molecular states outside the spectral profile of the pulses. This is due to the non-perturbative coupling between the light field and the ultracold atoms [24]. In order to excite into more deeply bound states the density of the atomic sample, and thereby the Franck-Condon overlap between the scattering wavefunction and

the excited molecular state, has to be significantly increased.

The use of a spectral cut to minimize spectral components near the atomic resonance has aided us in the experiment in two ways: Firstly, trap-loss due to ionization and radiation pressure was strongly suppressed. Secondly, coherent dynamics of the newly photoassociated molecules was revealed. By applying a linear chirp on the pump pulse we have been able to alter these coherent dynamics. The periodic oscillations can be attributed to coherent transient dynamics [24]. In addition, we see weak evidence for molecules formed by the ultrashort pulse, which have subsequently spontaneously decayed into the ground electronic state.

In order to observe vibrational wavepacket motion, ultrafast laser pulse control in the picosecond regime is needed [47], which fit to the time scale of vibrational dynamics at large internuclear distance. Combined with the high density this should allow to efficiently prepare deeply bound molecules in a pump-dump scheme.

VII. ACKNOWLEDGMENTS

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